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WITNESS my hand this  
Fifteenth day of July 2004

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AUSTRALIA  
Patents Act 1990

**PROVISIONAL SPECIFICATION**

**Applicant(s) :**

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH  
ORGANISATION

**Invention Title:**

METHOD OF PRODUCING TITANIUM

The invention is described in the following statement:

A METHOD AND APPARATUS FOR THE PRODUCTION OF METAL AND  
METAL COMPOUNDS

Field of the Invention

5       The present invention relates to a method and apparatus for the production of metal and metal compounds and, particularly, but not exclusively, to a method and apparatus for the production of titanium and titanium compounds.

10      Background of the Invention  
15      The following description mainly refers to the preparation of titanium and titanium compounds. Other metals can be made and manufactured by the method and apparatus of the present invention, however, and the invention is not limited to the production of titanium and titanium compounds.

20      Titanium minerals are found in the form of a very thermodynamically stable oxide ( $TiO_2$ ). Common processes for the production of titanium are the Kroll process and the Hunter process. The Kroll process requires the use of magnesium as a reducing agent to reduce  $TiCl_4$  (prepared from the oxide by a pre-process of chlorination) to produce the Ti metal. The Hunter process requires the use of sodium as the reducing agent. The problem here is that  $TiCl_4$  is still very thermodynamically stable so highly reactive reducing agents such as magnesium or sodium are required. Such highly reactive reducing agents are difficult and expensive to handle. As the magnesium chlorides in the case of the Kroll process are stable up to temperatures in excess of 1300 K, the product is often in the form of a Ti sponge mixed with  $MgCl_2$  and remnants of Mg and  $TiCl_2$ . To obtain pure Ti, the product requires extensive post-processing, including washing and melting in a vacuum arc furnace to remove all impurities. This contributes to the present high cost of the production of titanium.

According to existing technologies for production of titanium alloys such as Ti-Al and Ti-V-Al, sponges or ingots of the required metals in appropriate amounts are melted together, hence adding to the production cost. For 5 production of powder of these titanium alloys, further processing is usually required; further compounding the already high production cost.

Prior aluminium-based processes in the literature for direct production of Ti-Al alloys and inter-metallic 10 compounds are mostly centred on reduction of  $TiCl_4$  with aluminium monochloride gas  $AlCl$  (US patent application US 2002/0184971 and references therein). These processes require aluminium to be converted to  $AlCl$  at a temperature in excess of 1500 K prior to reacting  $AlCl$  with  $TiCl_4$  to 15 produce Ti-Al intermetallic compounds.

Over the past several decades, there have been extensive attempts made to replace the existing Kroll and Hunter technologies using techniques such as electrowinning, plasma-hydrogen and also aluminothermic 20 reduction.

Attempts have been made to use hydrogen plasma for reduction of titanium chloride in a plasma atmosphere, as possible replacement of the existing Kroll and Hunter processes. However, reduction of  $TiCl_4$  by hydrogen is 25 difficult due to unfavourable thermodynamic characteristics, as chlorine preferably reacts with titanium in the reverse reaction to produce titanium chlorides, hence degrading the quality of the produced Ti powder and limiting the efficiency of the hydrogen plasma route. In a recent process disclosed in US patent 30 5,935,293, a fast quench reactor was used to cool down the plasma in order to prevent recombination processes leading to formation of titanium chlorides. According to the description in US patent (5,935,293), the process is 35 highly energy expensive relative to the existing Kroll technology.

In a more recent process (G.Z. Chen, D.J. Fray and

T.W. Farthing, Nature, vol 407 (2000) 361), Chen et al. claim to have made titanium sponge directly from the oxide by reduction in a molten calcium chloride salt. Oxygen from the titanium oxide recombines with carbon at an anode 5 to form CO<sub>2</sub>. The composition of the titanium sponge produced corresponds to the composition of the starting minerals and may include impurities. The process is yet to be demonstrated on an industrial scale.

Also, there have been attempts to use Aluminium as a 10 reducing agent to remove chlorine out of TiCl<sub>4</sub> and for this purpose various techniques have been tried. High-temperature processes using Al as a reducing agent lead to formation of aluminium titanium alloys with somewhat uncontrollable quality. Aluminothermic reduction has also 15 been tried and Aluminium always ends up reacting with the titanium due to favourable thermodynamics for formation of Al-Ti alloys. Ti-Al are useful industrial products but an impediment to their use is associated with high cost of production as none of the existing technologies seem to be 20 economical for meeting requirements for manufacturing Ti-Al compounds at least for production of powdered compounds. Present technologies for making metallic Ti-Al alloys rely mostly on reacting titanium and aluminium metals at high temperature such as in electric arc 25 melting.

Attempts have been made to use aluminium as a reducing agent for TiCl<sub>4</sub> in plasma systems. For reduction of TiCl<sub>4</sub> using aluminium, the products would be in the form 30 of a solid phase titanium-aluminium intermetallic compounds mixed with aluminium chloride and some residual titanium dichloride. A description of various attempts using aluminium together with a description of the thermodynamics of the process are given by Murphy and Bing (High Temp: Chem. Processes, vol 3, 365-374, 1994). 35 Because of the strong affinity between aluminium and titanium, it has not been possible to produce pure titanium and titanium with a low aluminium content by

direct aluminothermic reduction of titanium chlorides.

Summary of the Invention

In accordance with a first aspect, the present  
5 invention provides a method for the production of titanium  
and/or titanium compounds, comprising the steps of mixing  
a precursor material of titanium trichloride with  
aluminium and heating the mixture to trigger reactions  
leading to the formation of aluminium chlorides and  
10 titanium and/or titanium compounds.

Titanium compounds may include titanium alloys and/or  
titanium/metal intermetallic compounds.

Preferably, the titanium compounds may include  
titanium-aluminium alloy and/or titanium-aluminium  
15 intermetallic compounds.

Preferably, the titanium trichloride is prepared from  
titanium chloride ( $TiCl_4$ ).

The precursor material may include titanium  
diochloride ( $TiCl_2$ ).

20 Preferably, the reaction conditions are arranged to  
favour the forward reaction to form the aluminium  
trichloride and titanium and/or titanium compounds, and  
reduce the reverse reaction. Preferably, this is achieved  
by removing aluminium trichloride from a reaction zone  
25 where the aluminium and precursor material are reacting.

The precursor materials may include other metals and  
products may include titanium alloys or intermetallic  
compounds. For example the precursor material may include  
30 vanadium subchlorides, such as vanadium trichloride and/or  
vanadium diochloride, and the products may include  
titanium-aluminium-vanadium alloy and/or intermetallic  
compounds and/or titanium-vanadium alloy and/or  
intermetallic compounds.

35 The precursor material may include zirconium halide,  
such as zirconium chloride, and the products may include a  
titanium-aluminium-zirconium alloy and/or intermetallic  
compounds and/or titanium-zirconium alloy and/or

intermediate compounds.

In accordance with a second aspect, the present invention provides a method for the production of a metal or metal compound, comprising the steps of mixing a precursor material of metal halide with aluminium and heating the mixture to a temperature sufficient such that the precursor material reacts with the aluminium, resulting in the formation of aluminium halide, and arranging the conditions to favour the forward reaction to form the aluminium halide and reduce the reverse reaction.

Preferably, the step of arranging reaction conditions includes the step of driving the aluminium halide away from a reaction zone where the aluminium and precursor material are reacting.

Preferably, the halide is a chloride.

Preferably, the metal halide is titanium halide and the product is titanium and/or titanium compounds.

In accordance with a third aspect, the present invention provides an apparatus for the production of a metal or metal compound, comprising a reaction vessel including a reaction zone within which a precursor material of metal halide is mixed with aluminium, the mixture being heated to a temperature sufficient such that the precursor material reacts with the aluminium to result in the formation of aluminium halide and a product, and a first condensation zone arranged to be operated to a temperature such that the aluminium halide condenses in the first condensation zone.

Preferably, the reaction vessel also includes a second condensation zone where a metal halide is arranged to condense. Preferably, the metal halide may be provided back into the reaction zone from the second condensation zone.

Preferably, the reaction zone operates at a temperature T<sub>1</sub> and the first condensation zone at a temperature T<sub>2</sub> which is lower than the temperature T<sub>1</sub>. The second condensation zone preferably operates at a

temperature T3 which is between T1 and T2.

The precursor material may be a material containing titanium as a component. The precursor material preferably includes titanium chloride.

5 Preferably, where the precursor material includes titanium chloride and where the apparatus includes a first condensation zone that operates to temperature T2, T2 is preferably below 200C, wherein gaseous aluminium trichloride emanating from the reaction zone is condensed.

10 Preferably, where the apparatus includes a second condensation zone, T3 is below 400C where and titanium trichloride products escaping from the reaction zone are recondensed at the second condensation zone. Preferably the second condensation zone is located between the reaction zone and the first condensation zone.

15 Preferably, the apparatus includes a heating arrangement for heating the precursor material. Preferably, openings are provided for the introduction of further gases for further reactions. Openings may also be provided to evacuate the vessel to a low pressure.

20 Preferably, the apparatus of this aspect of the invention is suitable for implementing the method of the first and second aspects of the invention discussed above.

25 In accordance with a fourth aspect, the present invention provides a method for the production of vanadium and/or vanadium compounds, comprising the steps of mixing a precursor material of vanadium trichloride with aluminium and heating the aluminium to trigger reactions leading to the formation of aluminium chlorides and vanadium and/or vanadium compounds.

30 In accordance with a fifth aspect, the present invention provides a method for the production of zirconium and/or zirconium compounds, comprising the steps of mixing a precursor material of zirconium trichloride with aluminium and heating the aluminium to trigger reactions leading to the formation of aluminium chlorides and zirconium and/or zirconium compounds.

In accordance with a sixth aspect, the present invention provides a method for the production titanium and/or titanium compounds, comprising the steps of mixing a precursor material including titanium tri-chloride with  
5 a reducing agent and heating the mixture to trigger reactions leading to the formation of chlorides and titanium and/or titanium compounds.

Brief Description of the Drawings

10 Features and advantages of the present invention will become apparent from the following description of embodiments thereof, by way of example only, with reference to the accompanying drawings, in which:

15 Figure 1 shows the Gibbs energy of formation of  $\text{AlCl}_3(\text{g})$ ,  $\text{TiCl}_3$  and  $\text{TiCl}_3 + \text{Ti-Al}$ ;

Figure 2 shows the total Gibbs free energy for reactions leading to formation of  $\text{Ti}(\text{s})$ ;

20 Figure 3 illustrates the equilibrium composition of  $\text{TiCl}_4$  - Hydrogen plasma at temperatures of between 300K and 5000K;

Figure 4 is a schematic diagram of an apparatus for implementing a process in accordance with an embodiment of the present invention;

25 Figure 5 is a schematic flow diagram showing production of Ti-Al ingot from  $\text{TiCl}_4$  starting materials; and

Figure 6 is a schematic diagram of a further embodiment of an apparatus for implementing a process in accordance with an embodiment of the present invention.

30

Description of Preferred Embodiments

The following description is of preferred embodiments of processes for producing metal compounds, including fine powder and ingots with specific compositions. The  
35 processes are useful for production of forms of metals such as Ti, V, Zr, together with alloys and intermetallic compounds of these metals with a controllable amount of

aluminium. For example, Ti-Al and Ti-V-Al can be made with accurate various aluminium content. The relative amounts of titanium chlorides and aluminium are determined by the required composition of end product. The process

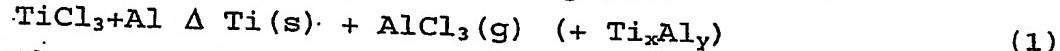
- 5 in one embodiment comprises the steps of preparing solid metal halides, mixing the halides with aluminium metal and heating the mixture to a temperature T<sub>1</sub> to trigger reactions leading to formation of aluminium chloride at a temperature (T<sub>1</sub>) above the boiling temperature of
- 10 aluminium chlorides and condensing the aluminium chlorides away from the reaction zone at a temperature T<sub>2</sub>, T<sub>2</sub> being less than T<sub>1</sub>. The driving of the aluminium chloride away from the reaction zone tilts the equilibrium of reaction in the forward direction i.e. to formation of aluminium
- 15 chloride and metal (and other products depending upon reaction conditions and components). For titanium compounds, titanium subchlorides preferably titanium trichloride TiCl<sub>3</sub> is produced from a precursor material of TiCl<sub>4</sub>, the TiCl<sub>3</sub> is mixed with aluminium and then heated to
- 20 a temperature above 300C so that AlCl<sub>3</sub> is formed in the gas phase and the AlCl<sub>3</sub> is condensed away from the reaction zone at a temperature below 200C, leaving in the reaction zone a powder of Ti containing a percentage of aluminium as required for the end product.

- 25 In one embodiment the process comprises the steps of heating a precursor material TiCl<sub>4</sub> in a plasma of argon-hydrogen mixtures to produce TiCl<sub>3</sub>, mixing the resulting TiCl<sub>3</sub> powder with aluminium and then heating the mixture to trigger the reaction. The reaction vessel should allow
- 30 for aluminium chloride to be continuously removed and condensed in a region away from the reaction zone of the titanium chloride and aluminium mixture. TiCl<sub>3</sub>, and aluminium in a powder or a lump form are mixed together in a vessel under inert gas or in vacuum. The mixture is
- 35 then heated to a temperature of several hundred degrees to trigger reaction between the two chemicals, leading to formation of AlCl<sub>3(g)</sub>, and the AlCl<sub>3</sub> is condensed elsewhere

in the vessel at a temperature below 200C.

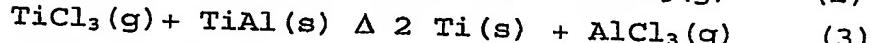
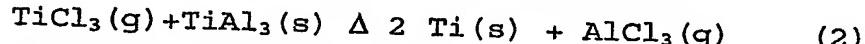
In a further embodiment, the process comprises the steps of heating predetermined amounts of material  $TiCl_4$  and aluminium to form  $TiCl_3$  and  $AlCl_3$ , heating the product mixture to a temperature above 300C and providing for  $AlCl_3$  to be evaporated from the reaction zone, driven away from the reaction and condensed away from the reaction zone at a temperature below 200C, adding further aluminium material to the product depending on the required composition, then heating the mixture under the same physical conditions to a temperature above 300C to trigger chemical reactions leading to formation of  $AlCl_3(g)$  whilst providing for the  $AlCl_3(g)$  to be condensed elsewhere in the vessel at a temperature below 200C:

Overall reaction between titanium subchlorides  $TiCl_3$  and Al occur in the following form:



Where Al is in the solid or liquid phase.

The presence of Ti and Al may lead formation of Ti-Al intermetallic compounds such as  $TiAl_3(s)$ ,  $TiAl(s)$  and  $Ti_3Al(s)$ . Then  $TiCl_3$  may react with aluminium according to the following simplified reactions:



Reactions 1-4 are driven in the forward direction by continuous removal of  $AlCl_3$  from the reaction zone. As a result, equilibrium is tilted to the right and the reaction proceeds until completion. We find that the reaction proceeds slowly at temperatures slightly above 200C under an argon atmosphere at 1 atm. The reaction becomes very rapid at temperatures above 500C as the Gibbs free energy of the total reaction becomes negative as seen in Figures 1 and 2. Figure 1 shows the Gibbs energy for  $AlCl_3$ ,  $TiCl_3$ , and  $TiCl_3+Ti-Al$ . Figure 2 shows the total Gibbs energy for reactions 1-4 leading to formation of solid titanium.

Because of the strong affinity between titanium and aluminium, the presence of Al and Ti may result in formation in titanium-aluminium intermetallic compounds  $Ti_xAl_y$ . For these compounds, the Gibbs energy of formation  $\Delta G_f$  is generally less than  $32\text{kJ.mole}^{-1}$  for all aluminium concentration up to 80% of the alloys (R.G.Reddy et al. J. Alloys and Compounds, vol 321 (2001) 223).

Figure 2 shows the variation with temperature of the total Gibbs energy for reaction leading to formation of  $AlCl_3(g)$  and  $Ti(s)$ , starting from  $TiCl_3$  and Al. Also shown in Figure 2, the total Gibbs energy for reaction leading to formation of  $Ti(s)$  and  $AlCl_3(g)$ , starting from  $TiCl_3$  and Ti-Al compounds. The total Gibbs free energy for Ti-AL is taken to be  $-32\text{kJ.mole}^{-1}$ , corresponding to the most stable alloy  $TiAl_3$  at 850K. As such, data presented in Figures 1 and 2 for the Ti-Al system corresponds to the least favourable reactions leading to formation of  $Ti(s)$ .

It is usually considered that chemical reactions proceed rapidly for negative values of the total Gibbs energy of the reaction. It is seen in Figure 2 that  $\Delta G$  is negative at temperatures above 800K (525C) for reaction 1. This is in excellent agreement with our observations showing rapid combustion reaction between  $TiCl_3$  and Al at a temperature of 500C, in argon in a sealed vessel at 1 atm. We find that as the temperature of the mixture  $TiCl_3$ -Al increases above 500C, a cloud of white fume moves from the reaction zone towards the cold region of the vessel where it recondenses forming solid  $AlCl_3$ . For reactions involving Ti-Al compounds, we find that in a closed vessel containing argon at 1 atm, reactions leading to formation of  $Ti(s)$  (reactions 2-3 and 4) seem to proceed rapidly at temperatures above 850C, at which the pressure in the vessel is about 3 atm.

Titanium chlorides may escape from the reaction zone or disproportionate during heating. Gaseous  $TiCl_3$  that may evaporate during the heating process reacts more readily with Al and further enhances formation of Ti compounds.

We find that only small quantities of less than a few percent of  $TiCl_3$  escapes the reaction zone, and it is recondensed in a region of the vessel at a temperature around 300K and introduced back into the reaction zone.

- 5  $TiCl_2$  that could be produced due to disproportionation reacts with Al compounds faster than  $TiCl_3$ , and enhances reactions leading to formation of  $Ti(s)$ . We find no evidence of major losses due to escape of  $TiCl_4$ , probably because  $TiCl_4$  reacts with Ti leading to formation of  $TiCl_2$ .
- 10 Our experimental observations suggest that for production of titanium with a high aluminium content, disproportionation reactions are of no significant impact on the efficiency of the process as we are able to account for most of the Ti in the feedstock materials. For
- 15 production of titanium with a low aluminium content, the initial amount of aluminium used is less than the stoichiometric amount needed to remove all the chlorine from the  $TiCl_3$  materials. The excess titanium chloride remaining after depletion of available aluminium is
- 20 evaporated from the product and condensed elsewhere for reprocessing.

Production of  $TiCl_3$  can be carried out from  $TiCl_4$  using a hydrogen plasma route or through reduction with aluminium. Production of  $TiCl_3$  in a hydrogen plasma, known as the Huel process has been used in industry for production of catalyst for several decades. Figure 3 shows the composition of  $TiCl_4$ -Hydrogen plasma at temperature between 300K and 5000K. It is seen  $TiCl_4$  can be converted into solid  $TiCl_3$  by reacting it with hydrogen in a plasma. It is also seen that the conversion rate is almost 100%. The energy cost for synthesis of solid  $TiCl_3$  is very low as the overall reaction leading to  $TiCl_3$ :

$TiCl_4(g) + (1/2)H_2 \rightleftharpoons TiCl_3(s) + HCl$  with  $\Delta H = 50$  KJ/mole.

- 35 For reduction of  $TiCl_4$  with Aluminium, the process is usually carried out in closed vessel containing appropriate amounts of  $TiCl_4$  and Al at a temperature above

200C, leading to formation of a mixture of  $TiCl_3$  and  $AlCl_3$ . Pure  $TiCl_3$  is obtained from the mixture by distillation at temperature above 200C and allowing  $AlCl_3$  to condense elsewhere.

5 For the process disclosed here, production of titanium-aluminium compounds is made by mixing subchlorides, preferably  $TiCl_3$ , with aluminium in a powder form, preferably compacting the mixture, placing the materials in a vessel under vacuum or in an inert  
10 atmosphere and heating the mixture. For processing under vacuum,  $AlCl_3$  formed due to reactions described above is driven into a different part of the vessel at a temperature below 200K. The heating continues until the reactions proceed to completion or until complete  
15 depletion of available titanium subchlorides and/or aluminium

Figure 4 shows a simple system used to make Ti-Al alloys with Al contents between 99% and less than 1%. For this configuration Ohmic heating is used to drive the  
20 reactions. A mixture of  $TiCl_3$  and Al, 1, is placed into a crucible 2. The conducting crucible 2 is connected to a current carrying rods 3. The crucible is located inside a vessel 4 held at a temperature below 200C under an argon atmosphere. For the arrangement in Figure 4,  $AlCl_3$ ,  
25 evaporated from the reaction zone in the container 2, recondenses on the internal walls of the vessel 4.

Heating of the  $TiCl_3$ -Aluminium mixture can be made using various means. For example, the aluminium can be made to melt followed by the  $TiCl_3$  dropped into the melt  
30 and the mixture is stirred until all the chlorine or all the available aluminium is driven out in the form of aluminium chloride.  $TiCl_3$  that may escape with the chloride may be made to condense in a different part of the vessel and then put back in the reaction zone.

35 Alternatively, the  $TiCl_3$  and an aluminium powder whose relative mass compared to the  $TiCl_3$  amount depends on the composition of the required product, are introduced

into a vessel as described above and then heated until the reaction is complete.

For these processes described above the product is in the form of a fine powder. The powder may be discharged from the vessel at the completion of chemical reactions in the reaction zone for further processing. Alternatively, the powder may be further processed in-situ for production of materials such as TiH<sub>2</sub>. Alternatively the powder may be heated in-situ to make coarse grain powder. In a different embodiment the powder may be compacted and/or heated in-situ and then melted to produce ingot.

Figure 5 is a schematic diagram illustrating the integration of the process described here into a full system for production of ingot.

In one embodiment of the process in accordance with the present invention, a precursor material is mixed with aluminium in a powder or lump form and heated to a temperature T<sub>1</sub>, in this embodiment by raising the temperature of the container. The precursor material, namely TiCl<sub>3</sub>, is in a powder form. The second precursor materials, namely aluminium, may be in the form of a liquid, or a lump solid or a powder. The materials are placed in a container and heated to trigger reactions between the Aluminium and the chlorine from the TiCl<sub>3</sub> compounds. In this embodiment the products are in a powder form that may be discharged out of the vessel or may be further reacted with reagents, in a solid, liquid or gas form, in the form of other materials introduced in the reaction zone during or after processing with aluminium.

Referring to Figure 4, there is schematically illustrated an example of a system that may be used to carry out a process in accordance with an embodiment of the present invention. A Tantalum container 2 is used to enclose the TiCl<sub>3</sub>-Al mixture. The container 2 is enclosed in a gas tight cylinder 4 to prevent reacting gases from entering the chamber during the reaction. The Tantalum

container 2 is connected to a power supply capable of delivering high current. Current is passed through the Tantalum container to increase its temperature together with its contents to bring the reaction between the  $TiCl_3$  and the Al to completion. The cylinder 4 may be connected to a pumping system maintaining a low-pressure environment in the cylinder and driving  $AlCl_3$  compounds away from the reaction zone. Alternatively, the cylinder may be sealed while heating of the  $TiCl_3$ -Al mixture takes place.

A further embodiment of the apparatus is illustrated in Figure 6. The same reference numerals have been used for components equivalent to the components of the Figure 4 embodiment. No further description will be given of these components. The reaction vessel of Figure 6 includes an arrangement 5 which forms a second condensation zone. The second condensation zone is held at a temperature  $T_3$  which is between the temperature of the reactance 1,  $T_1$ , and the temperature,  $T_2$  of the wall of the vessel 4. In operation, titanium trichloride recondenses in the second condensation zone 5 and aluminium trichloride recondenses on the walls of vessel 4. The second condensation zone 5 is arranged so that condensed titanium trichloride returns to the reaction zone 1.

Parameters influencing reactions in the reaction zone described above include the pressure in the reaction vessel and the temperature of the reaction zone. We find that for operation under low pressure, a lower temperature is required to drive the reaction as  $AlCl_3$  is removed faster from the reaction zone and  $TiCl_3$  species become more volatile and more active triggering reactions with Aluminium.

Production of Ti metal and Ti-Al alloys and intermetallic compounds may be carried out using the current process starting from a  $TiCl_4$  feedstock materials as follows.

Reduction of TiCl<sub>4</sub> using Aluminium:

TiCl<sub>4</sub> and aluminium metal in appropriate amounts are introduced into a closed vessel under an argon atmosphere.

- 10 The vessel is then heated to a temperature above 200C to  
5 form a mixture of TiCl<sub>3</sub> and AlCl<sub>3</sub>. The TiCl<sub>3</sub> powder is then extracted from the mixture by distillation as described before. The TiCl<sub>3</sub> powder is then mixed with more aluminium if required and processed utilising an apparatus such as described above in relation to Figure 4.

Reduction of TiCl<sub>4</sub> using hydrogen and Aluminium:

The precursor materials of TiCl<sub>4</sub> may be fed into a plasma-processing unit operating with argon and hydrogen gas to produce TiCl<sub>3</sub>. Then, products at the exit of the

- 15 plasma processing system may travel through a filter to separate TiCl<sub>3</sub> from the gas stream and the resulting TiCl<sub>3</sub> powder is then moved into a processing chamber where it is mixed with an appropriate amount of aluminium, depending on the required composition of the end product. The TiCl<sub>3</sub> powder is then mixed with aluminium and processed  
20 utilising an apparatus such as described above in relation to Figure 4 or Figure 6. At the completion of the reaction, the materials can be discharged from the reaction vessel for use in manufacturing. Alternatively,  
25 the powder can be consolidated in-situ and then melted to produce ingots.

Gases from the plasma system may be re-used after separation and cleaning.

The method described here may also be used for  
30 production of metals and metal alloys by mixing metal halide or a mixture of metal halides (chlorides, bromides, iodides and fluorides) and carry out the process as described above for the TiCl<sub>4</sub>. For example, zirconium and zirconium alloys may be produced using the same  
35 procedures described above for Ti and Ti alloys respectively. For zirconium-based products, the starting material is zirconium chloride. Other examples of metals

that can be produced using the present process include vanadium and its alloys and intermetallic compounds. Furthermore, hydrides can also be produced by heating the resulting powder materials in the presence of hydrogen.

- 5 For example, for production of Titanium hydride,  $TiH_2$ , the process is first carried out as described above to produce Ti powder and then Hydrogen is injected into the reaction vessel while the powder is maintained at high temperature, resulting in formation of  $TiH_2$ .
- 10 The present process may be used for production of powders with a controlled particle size of various compositions including compounds of pure metal, oxides, nitrides of elements such as Ti, V and zirconium as described above for titanium. Many other materials may be
- 15 produced by this chemical process.

Modifications and variations as would be apparent to a skilled addressee are deemed to be within the scope of the present invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for the production of titanium and/or titanium compounds, comprising the steps of mixing a precursor material of titanium trichloride with aluminium and heating the mixture to trigger reactions leading to the formation of aluminium chlorides and titanium and/or titanium compounds.
2. A method in accordance with claim 1, comprising the step of arranging the conditions to favour a forward reaction to form the aluminium chlorides and titanium and/or titanium compounds, and reduce the reverse reaction.
3. A method in accordance with claim 2, wherein the step of arranging the reaction conditions includes the step of driving aluminium chlorides away from a reaction zone where the aluminium and precursor material are reacting.
4. A method in accordance with claims 1, 2 or 3, comprising the step of preparing the titanium trichloride precursor material from titanium chloride ( $TiCl_4$ ).
5. A method in accordance in with claim 4, comprising the step of preparing the titanium trichloride by reduction of  $TiCl_4$  using aluminium.
6. A method in accordance with claim 4, wherein the step of preparing the titanium trichloride is carried out by heating  $TiCl_4$  in a plasma or argon-hydrogen mixture.
7. A method in accordance with any one of claims 2 to 6, wherein the aluminium chloride is condensed away from the reaction zone at a lower temperature than the temperature of the reactants in the reaction zone.
8. A method in accordance with any of claims 3 to 7, wherein any titanium trichloride escaping the reaction zone is condensed at a temperature different from that in reaction zone.
9. A method in accordance with claim 8, comprising the furthest step of returning the condensed titanium

trichloride to the reaction zone.

10. A method in accordance with any one of the preceding claims, wherein the precursor material includes vanadium subchlorides, and a product of the reaction is an alloy or intermetallic complex including titanium or vanadium.

5 11. A method in accordance with any one of the preceeding claims, comprising the further step of adding a reagent to the product of the reaction to produce a further product.

12. A method in accordance with any one of claims 3 to 8, 10 wherein the product is titanium powder.

13. A method in accordance with claim 11, comprising a step of heating the titanium powder in the presence of hydrogen to produce titanium hydride.

14. A method in accordance with any one of the preceeding 15 claims, wherein the precursor material is mixed with a powder of reducing aluminium metal.

15. A method in accordance with any one of claims 1 to 12, wherein the precursor materials are added to a molten pool of the reducing aluminium.

20 16. A method in accordance with any one of claims 1 to 10, wherein the precursor material includes zirconium subchlorides, and a product of the reaction is an alloy or intermetallic complex including zirconium and vanadium.

17. A method of producing titanium, comprising the steps 25 of heating a precursor material of  $TiCl_4$  in a plasma argon-hydrogen mixture to produce  $TiCl_3$ , mixing the resulting  $TiCl_3$  powder with aluminium and heating the mixture to produce Ti and  $AlCl_3$ .

18. A method of producing titanium, comprising the steps 30 of heating  $TiCl_4$  and aluminium to form  $TiCl_3$  and  $AlCl_3$ , heating the mixture to a temperature above 300C and providing for  $AlCl_3$  to be evaporated from the reaction zone, adding further aluminium to the mixture, and heating the mixture to a temperature above 400C to lead to 35 formation of  $AlCl_3$  and Ti, the  $AlCl_3$  being removed from the reactant.

19. An apparatus for the production of a metal or metal

- compound, comprising a reaction vessel including a reaction zone within which a precursor material of metal halide is mixed with aluminium, the mixture being heated to a temperature sufficient such that the precursor
- 5 material reacts with the aluminium to result in the formation of aluminium halide and a product, and a first condensation zone arranged to be operated to a temperature such that the aluminium halide condenses in the first condensation zone.
- 10 20. An apparatus in accordance with claim 18, also providing a second condensation zone arranged to condense metal halide escaping the reaction mixture.
21. An apparatus in accordance with claim 19, the second condensation zone being arranged to return condensed metal halide to the reaction of the mixture.
- 15 22. A method for the production of a metal or metal compound, comprising the steps of mixing a precursor material of metal halide with aluminium and heating the mixture to a temperature sufficient such that the
- 20 precursor material reacts with the aluminium, resulting in the formation of aluminium halide, and arranging the conditions to favour the forward reaction to form the aluminium halide and reduce the reverse reaction.
- 25 23. A method in accordance with claim 21, wherein the step of arranging the reaction conditions include the step of driving aluminium halide away from a reaction zone where the aluminium and precursor material are reacting.
24. A method in accordance with claim 21 or claim 22, wherein the metal halide is titanium tri-chloride, and a
- 30 product of the reaction includes titanium.
25. A method for the production of vanadium and/or vanadium compounds, comprising the steps of mixing a precursor material of vanadium subchloride with aluminium and heating the mixture to trigger reactions leading to
- 35 the formation of aluminium halides and vanadium and/or vanadium compounds.
26. A method for the production of zirconium and/or

zirconium compounds, comprising the steps of mixing the precursor material of zirconium subhalide with aluminium and heating the mixture to trigger reactions leading to the formation of aluminium halide and zirconium and/or zirconium compounds.

- 5        27. A method for the production of titanium and/or titanium compounds, comprising the steps of mixing a precursor material including titanium tri-chloride with a reducing agent and heating the mixture to trigger  
10      reactions leading to the formation of chlorides and titanium and/or titanium compounds.

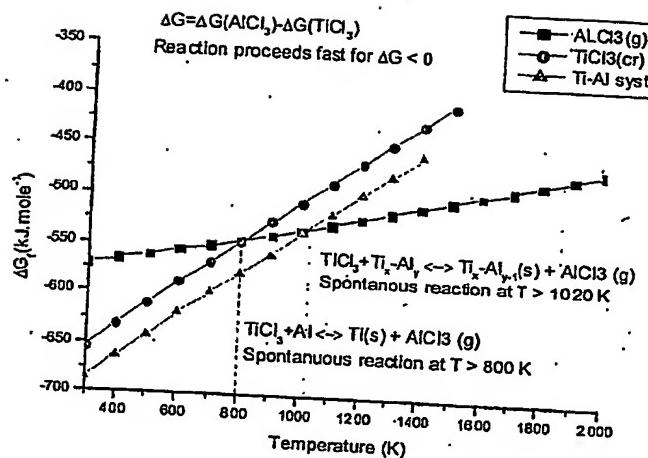
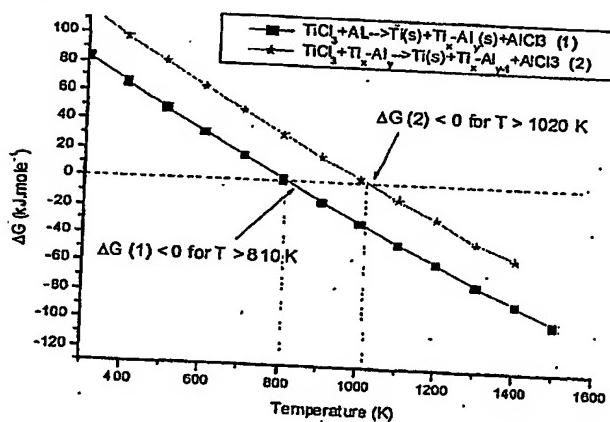
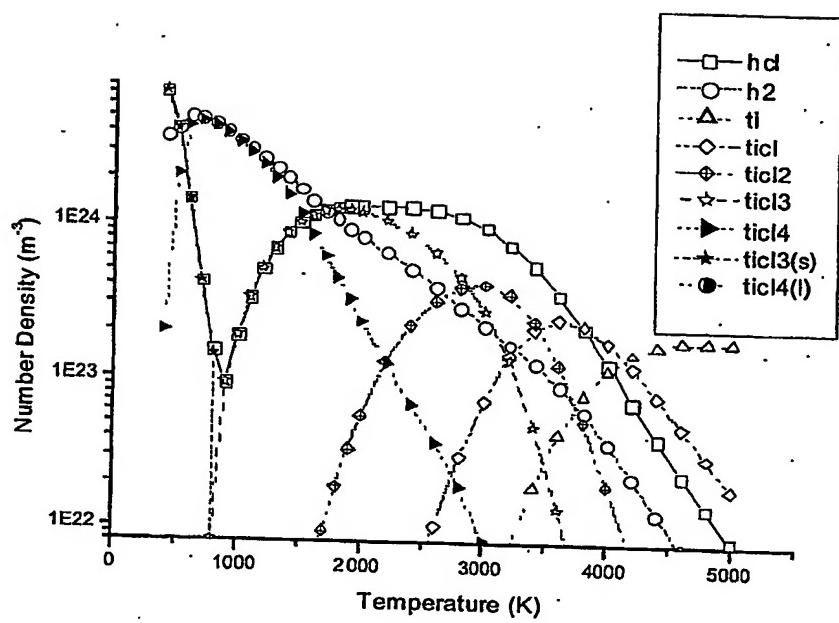


Figure 1: Gibbs energy of formation for  $\text{AlCl}_3(\text{g})$ ,  $\text{TiCl}_3$  and  $\text{TiCl}_3 + \text{Ti-Al}$ .



Total Gibbs free energy for reactions leading to formation of  $\text{Ti}(\text{s})$

FIGURE 2.



**Figure 3: Equilibrium composition of Hydrogen-TiCl<sub>4</sub> plasma at 1 atm. 1 mole of TiCl<sub>4</sub> and 1 mole of H<sub>2</sub>.**

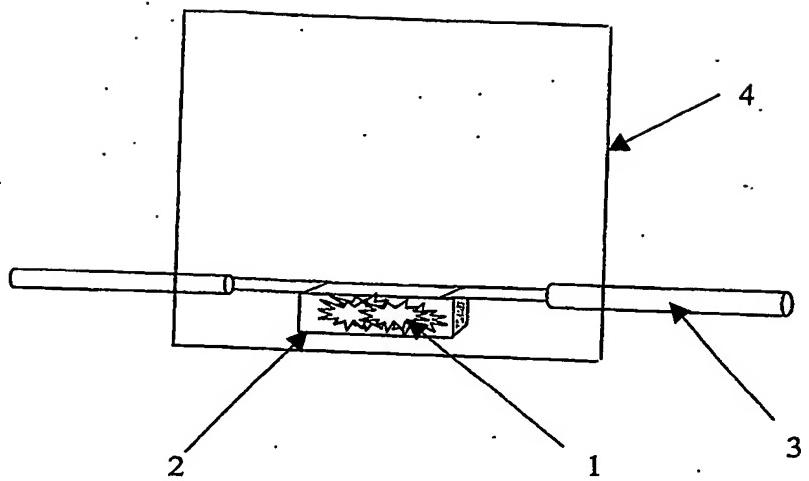
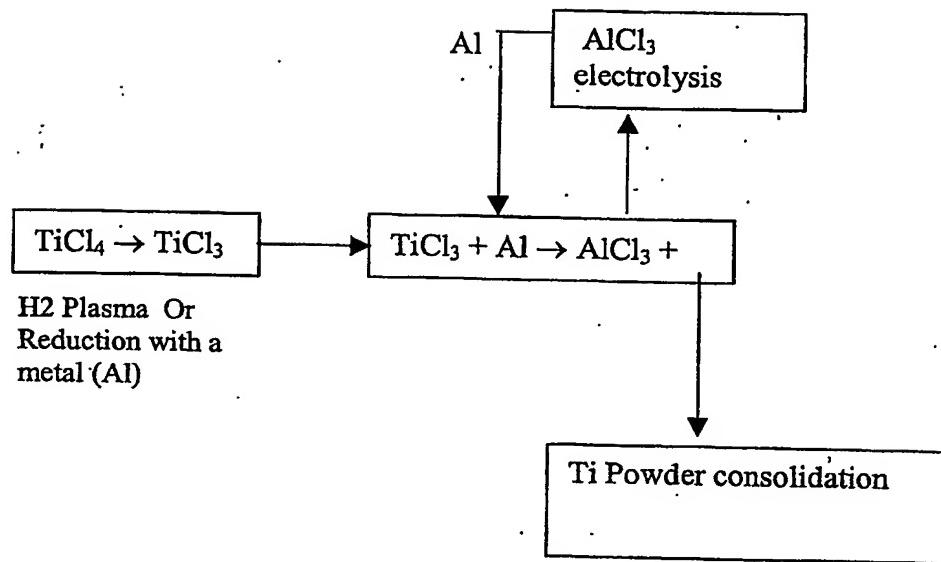


Figure 4: A schematic diagram of an apparatus for carrying out the process.



A schematic diagram illustrating production of Ti-Al ingot starting from  $\text{TiCl}_4$ .

FIGURE 5

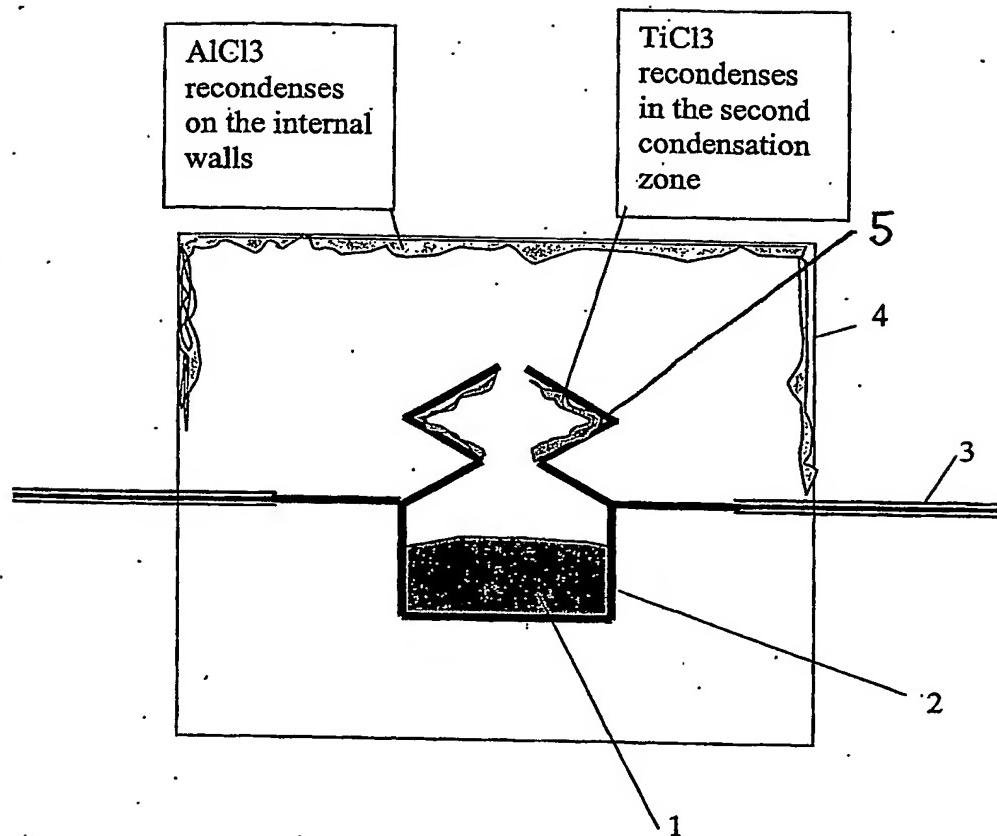


FIGURE 6